

PATENT SPECIFICATION

NO DRAWINGS

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855,009



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International Classification:—C08f.

COMPLETE SPECIFICATION

Improvements in or relating to Ion-Exchange Resins

We, UNITED KINGDOM ATOMIC ENERGY AUTHORITY, of London, a British Authority, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

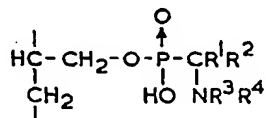
This invention relates to ion-exchange resins containing phosphonate groups.

The object of the invention is to provide improved ion-exchange resins containing substituted-aminomethyl phosphonate groups and having an amphoteric character.

Such improved resins may be derived from polymers which already comprise phosphonate groups, for example polymers of diallyl hydrogen phosphonate.

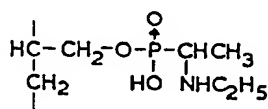
Diallyl hydrogen phosphonate, which is tautomeric with diallyl phosphite, and which can be prepared in pure form by the method described in co-pending application No. 18375/54 (Serial No. 778,077), may be polymerised by conventional means.

In accordance with the invention an amphoteric ion-exchange resin comprises a monoallyl substituted - aminomethyl phosphonate polymer having a structural unit formula represented by:



where R^1 and R^2 are alkyl groups or hydrogen, and R^3 and R^4 are alkyl or aryl groups or hydrogen or together with the nitrogen atom form a piperidine or morpholine group, but are not both hydrogen.

More particularly, said ion-exchange resin comprises a monoallyl alpha-ethylamino-ethyl phosphonate polymer, having the structural unit formula represented by:



Also in accordance with the invention, a method of preparing an ion-exchange resin consisting of a monoallyl substituted-aminomethyl phosphonate polymer comprises the steps of causing a polymer of diallyl hydrogen phosphonate to react with a mixture of an aliphatic aldehyde or ketone and a primary or secondary amine, or with a reaction product of said aldehyde or ketone and said amine, and then partially hydrolysing the product to yield an amphoteric polymer.

More particularly a method of preparing an ion-exchange resin consisting of a monoallyl alpha-ethylamino-ethyl phosphonate polymer comprises reacting a polymer of diallyl hydrogen phosphonate with acetaldehyde-ethylimine, and partially hydrolysing the product to yield an amphoteric polymer.

The reaction of monomeric hydrogen phosphonate diesters with mixtures or reaction products of an aldehyde or ketone and an amine has been described by Fields in "Journal of the American Chemical Society," 1952, p 1528—31. It is believed that similar reactions occur with the polymeric allyl hydrogen phosphonates.

Examples of suitable aldehydes and ketones are: formaldehyde, acetaldehyde, propaldehyde, and acetone. Suitable primary amines are: methylamine, ethylamine and aniline; and suitable secondary amines are: dimethylamine, diethylamine, N-ethylaniline, piperidine, and morpholine. Reaction products of aldehydes or ketones with primary amines are the aldimines and ketimines, having the general formula: $\text{R}^1\text{R}^2\text{C}=\text{NR}^3$, such as: acetaldehyde-ethylimine, propaldehyde-ethylimine, and acetone-ethylimine. Reaction pro-

ducts of aldehydes or ketones with secondary amines are the alpha-alkylolamines, having the general formula: $R^1R^2C(OH)-N R^3R^4$, such as methylol-diethylamine, $CH_2(OH)-N(C_2H_5)_2$, formed by reaction of formalde-

A particular method of preparing an ion-exchange resin in accordance with the invention will now be described in the following example.

EXAMPLE:

A. Preparation of diallyl hydrogen phosphonate polymer.

Diallyl hydrogen phosphonate 40 g, and dibenzoyl peroxide 0.15 g, were heated together in a sealed tube at 60° C for 7 days to give a brittle, transparent polymer. The polymer was crushed, washed repeatedly with ethanol, and dried.

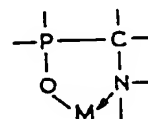
B. Preparation of amino-alkyl phosphonate polymer.

To 40 g of dry polymer obtained from A was added 30 g acetaldehyde-ethylimine. The polymer imbibed all of the imine within a few minutes, after which a considerable rise in temperature occurred, followed by reflux of the imine. Reflux continued for 10 minutes, after which the product was allowed to cool and left in a stoppered flask for 48 h. The product was then purified by refluxing repeatedly with acetone.

C. Preparation of amphoteric polymer.

30 g of the purified product from C was refluxed with 100 ml of 10% alcoholic potash for 3 h, and then filtered and washed with water. The product was an amphoteric ion-exchange material with a high affinity for ferric and cupric ions.

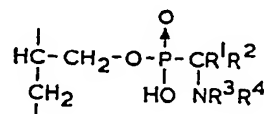
The ion-exchange resins of the invention have a greater affinity for divalent transition metal ions, than for uranyl ions, and may have possible use in the separation of uranium from other metals. Their behaviour towards metal ions is similar to that of the analogous alpha-amino carboxylic acid polymers described by Gregor, et al., in "Industrial & Engineering Chemistry," 1952, vol. 44, p. 2834. It is believed that 5-membered ring complexes are formed, having the structure represented by:



where M is the metal ion.

WHAT WE CLAIM IS:—

1. An amphoteric ion-exchange resin comprising a monoallyl substituted-aminomethyl phosphonate polymer having a structural unit formula represented by:



where R^1 and R^2 are alkyl groups or hydrogen, and R^3 and R^4 are alkyl or aryl groups or together with the nitrogen atom form a piperidine or morpholine group, but are not both hydrogen.

2. An amphoteric ion-exchange resin as claimed in claim 1, in which R^1 is hydrogen, R^2 is a methyl group, R^3 is hydrogen, and R^4 is an ethyl group.

3. An amphoteric ion-exchange resin as claimed in claim 1 or Claim 2, substantially as hereinbefore described.

4. A method of preparing an ion-exchange resin as claimed in claim 1, comprising the steps of causing a polymer of diallyl hydrogen phosphonate to react with a mixture of an aliphatic aldehyde or ketone and a primary or secondary amine, or with a reaction product of said aldehyde or ketone and said amine, and then partially hydrolysing the product to yield an amphoteric polymer.

5. A method of preparing an ion-exchange resin as claimed in claim 2, comprising the steps of reacting a polymer of diallyl hydrogen phosphonate with acetaldehyde-ethylimine, and partially hydrolysing the product to yield an amphoteric polymer.

6. A method of preparing an ion-exchange resin substantially as described in the foregoing example.

S. C. BARTLETT,
Chartered Patent Agent,
Agent for Applicants.

PROVISIONAL SPECIFICATION

Improvements in or relating to Ion-Exchange Resins

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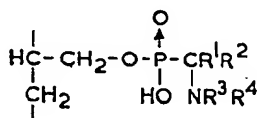
This invention relates to ion-exchange resins derived from polymers of diallyl hydrogen phosphonate.

The object of the invention is to provide an improved ion-exchange resin derived from said polymers and having an amphoteric character.

Diallyl hydrogen phosphonate, which is tautomeric with diallyl phosphite, and which can be prepared in pure form by the method

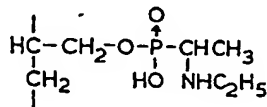
described in copending application No. 18375/54 (Serial No. 778,077), may be polymerised by conventional means.

- 5 In accordance with the invention an amphoteric ion-exchange resin comprises a monoallyl substituted - aminomethyl phosphonate polymer, having the structural unit formula represented by:



- 10 where R^1 , R^2 are alkyl groups or hydrogen, and R^3 , R^4 are alkyl or aryl groups or hydrogen or together form a cyclic group, but are not both hydrogen.

- 15 More particularly, said ion-exchange resin comprises a monoallyl alpha-ethylamino-ethyl phosphonate polymer, having the structural unit formula represented by:



- 20 Also in accordance with the invention, a method of preparing said ion-exchange resin comprises the steps of causing a polymer of diallyl hydrogen phosphonate to react with a mixture of an aliphatic aldehyde or ketone and a primary or secondary amino, or with
- 25 a reaction product of said aldehyde or ketone and said amine, and then partially hydrolysing the product to yield an amphoteric polymer.

- 30 More particularly a method of preparing an ion-exchange resin consisting of a monoallyl alpha-ethylamino-ethyl phosphonate polymer comprises reacting a polymer of diallyl hydrogen phosphonate with acetaldehyde-ethylimine, and partially hydrolysing the product to yield an amphoteric polymer.

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- 50 of aldehydes or ketones with primary amines

are the aldimines and ketimines, having the general formula: $\text{R}^1\text{R}^2\text{C}=\text{NR}^3$, such as: acetaldehyde-ethylimine, propaldehyde-ethylimine, and acetone-ethylimine. Reaction products or aldehydes or ketones with secondary amines are the alpha-alkylolamines, having the general formula: $\text{R}^1\text{R}^2(\text{COH})-\text{N}-\text{R}^3\text{R}^4$, such as methylol-diethylamine, $\text{CH}_2(\text{OH})-\text{N}(\text{C}_2\text{H}_5)_2$, formed by reaction of formaldehyde and diethylamine.

A particular method of preparing an ion-exchange resin in accordance with the invention will now be described in the following example.

EXAMPLE.

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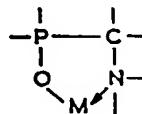
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C. Preparation of amphoteric polymer.

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The ion-exchange resins of the invention have a greater affinity for divalent transition metal ions, than for uranyl ions, and may have possible use in the separation of uranium from other metals. Their behaviour towards metal ions is similar to that of the analogous alpha-amino carboxylic acid polymers described by Gregor, et al., in "Industrial & Engineering Chemistry," 1952, vol. 44, p. 2834. It is believed that 5-membered ring complexes are formed, having the structure represented by:



where M is the metal ion.

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